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A Compact, Low-Power, Cantilever-Based Sensor Array for Chemical Detection

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ABSTRACT

A compact and low-power cantilever-based sensor array has been developed and used to detect various vapor analytes. This device employs sorptive polymers that are deposited onto piezoresistive cantilevers. We have successfully detected several organic vapors, representing a breadth of chemical properties and over a range of concentrations. Comparisons of the polymer/vapor partition coefficient to the cantilever deflection responses show that a simple linear relationship does not exist, emphasizing the need to develop an appropriate functional model to describe the chemical-to-mechanical transduction that is unique to this sensing modality.

Keywords: chemical sensors, microcantilevers, polymers, piezoresistive, vapor detection

1 INTRODUCTION

The development of miniature sensor technologies, popularly known as "electronic noses" or "electronic tongues", has been driven by the desire to detect chemical and biological agents of interest in the vapor and liquid phases. In most of the intended applications, including the detection of chemical weapons (e.g., nerve and blister agents) and the monitoring of air quality in closed or controlled environments (e.g., manned spacecraft), the sensors must actively detect analytes at concentrations of a few parts-per-million (ppm) or less, while simultaneously operating unobtrusively as robust, self-contained units with modest power consumption [1,2].

Currently, commercial handheld sensors for chemical agents of interest are almost exclusively based on ion mobility spectrometry (IMS) [3]. These portable devices, which can afford detection of nerve and blister agents down to tens and hundreds of parts per billion (respectively), nevertheless possess several disadvantages, including: 1) the requirement of complex, power-hungry electronics to produce the uniform electric fields needed within their ion drift channels, which are inches in length; 2) the difficulty in miniaturizing ionization sources that must produce low kinetic energy ions necessitated by the reduced drift volumes [4].

The clear need for simple, low-power, miniaturizable chemical sensors has driven the development of polymer-based sensor arrays that utilize nonspecific adsorption of vapor-phase analytes for detection. A number of different transducer modalities have been investigated, including acoustic wave devices (e.g. surface acoustic wave or SAW, and quartz crystal microbalance or QCM), and chemi-resistive conductive polymer composites, as well as microfabricated cantilevers and membranes [5-7]. Sensor elements based on microcantilevers are intrinsically microscopic in size and can be readily fabricated in dense arrays by current nanofabrication methods [8]; such sensors are comparatively inexpensive, and complete sensor packages could potentially approach the size required for personal dosimeters.

To this end we have developed a compact and low-power, cantilever-based sensor array, which we have used to detect various vapor analytes. This device is based on the static deflection of microcantilevers, which is measured via changes in piezoresistance rather than with a conventional beam-deflection method. The bending of the cantilevers is induced by polymeric coatings, which undergo swelling upon the reversible sorption of analyte vapors. By incorporating the signal transducer into the microcantilevers themselves, reliance on external optics is eliminated and the size and power consumption of the sensor is significantly reduced.

In addition to device fabrication and testing we are also currently investigating theoretical approaches to selecting polymers based on their predicted sorption of the analytes of interest; our results indicate that the partition coefficient, a simple thermodynamic interaction parameter, is insufficient *per se* in predicting cantilever deflection response resulting from penetrant diffusion into the polymers.

2 DEVICE DESCRIPTION

The current device consists of an array of eight piezoresistive cantilevers, six of which are functionalized and two assigned as references. Each cantilever (120 μm × 50 μm × 0.5 μm) is composed of silicon nitride encapsulating a boron-doped, polysilicon layer offset from the strain-neutral plane [9]. These cantilevers correspond to a pair of Canti^{TM}Chip4 sensor arrays, manufactured by Cantion A/S, Denmark [10]. The use of differential signals with respect to the reference cantilevers permits common-mode rejection of noise attributed to thermal drift and the binding of analytes to any non-functionalized surfaces, dramatically increasing the stability and repeatability of sensor response.

The sensor elements currently consist of thermoplastic (i.e., non-crosslinked) polymer coatings applied to the backside of each microcantilever. Upon exposure to gas-phase analytes, the swelling of these functional coatings

induces an alteration of the interfacial surface stress between the polymer layer and the cantilever; the resultant bending creates changes in piezoresistance that are readily detected (Fig. 1). To ensure sensitivity to a diversity of analytes, a series of six polymers have been selected with a range of physical and chemical characteristics, including polarity, glass transition temperature T_g, and total Hansen solubility parameter SP_O. Since piezoresistive cantilevers possess spring constants that are approximately 10 times greater than conventional optical cantilevers, the use of polymers with T_g much greater than the operating temperature helps offset the intrinsic loss in sensitivity by providing more rigid coatings capable of exerting greater stresses upon the cantilever during analyte sorption compared to similar elastomeric films. While the diffusion characteristics of glassy versus rubbery polymers are generally unfavorable, our use of the former does not appear to severely retard the sensor response times (Section 3.2) while significantly increasing the robustness of the sensor.

3 CHEMICAL VAPOR DETECTION

To test our sensor array, characteristic response patterns of differential deflection voltages were measured for a number of volatile organic compounds (VOC): 1,4-dioxane, toluene, ethyl acetate, acetone, acetonitrile, methylene chloride, methanol, ethanol, and isopropanol. Arbitrary concentrations (2000 to 50,000 ppm) were selected to help probe the dynamic range of the sensor. All of the VOCs were prepared by bubbling dry, flow-regulated air through each solvent to obtain a saturated vapor, and mixing with a parallel air channel to achieve the desired concentration; the resulting mixture was then flowed directly over the cantilever array at a rate of 155 to 220 standard cubic centimeters per minute (sccm) until maximum cantilever deflection was achieved for all six functionalized levers.

Two types of experiments were conducted: 1) systematic training of the sensor array to create a library of chemical signatures, consisting of the collective deflection responses from the six, polymer-coated cantilevers; 2) subsequent detection tests conducted in near-real-time and referenced directly to the signature library, to evaluate the response performance (including reproducibility) of the sensor.

Each response of the sensor array to an analyte is represented by a data point in a six-dimensional (6-D) space, with each coordinate directly corresponding to one of the six polymer sensor elements. To better visualize the analyte response patterns, a non-parametric data reduction was applied using principal components analysis (PCA); this method linearly transforms each of the original 6-D data points in such a way that the leading coordinate represents the maximum statistical variation in the original data, with each successive coordinate expressing a diminishing fraction of the variance. Since most of the variance is lodged in the first two coordinates (called the principal components, PC), the original data can be rendered as two-dimensional (2-D) plots while preserving almost all of the meaningful information in the raw data.

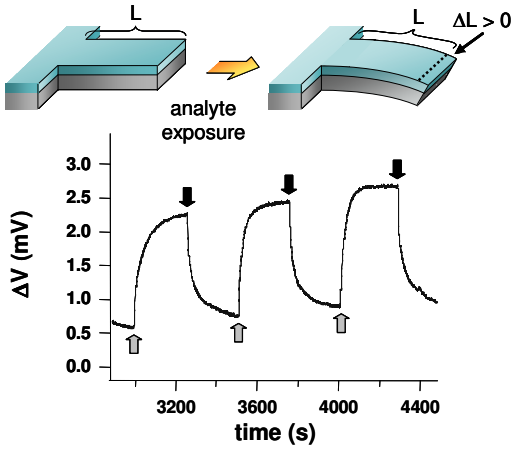

Fig. 1. Cartoon of transduction mechanism and data from a single cantilever exposed to analyte. The gray and black arrows indicate when the analyte vapor was introduced and removed, respectively.

3.1 Analyte Response Data and Analysis

In Fig. 2, a 2-D PCA plot is shown of the nine analyte signatures; each spatially discrete cluster in the PCA subspace, comprised of several hundred data points, corresponds to one of the VOCs at a particular concentration. The numbered clusters are identified as: absence of analyte (0), 1,4-dioxane (1), toluene (2), ethyl acetate (3), acetone (4), acetonitrile (5), methylene chloride (6), methanol (7), ethanol (8), and isopropanol (9). Although the data is limited, it is clear from the PCA analysis that the VOCs tested, which include several prototypical classes of compounds (ether, aromatic, ester, ketone, nitrile, and alcohol), are mutually differentiable. Note that the PCA plot can be extended to the third principal component, if necessary, to increase analyte discrimination; however, for this set of data PC 3 contains only ~0.27% of the statistical variance, so contributes little to cluster separation in the third dimension.

It is interesting to note that the alcohols occupy the same general region of the PCA subspace at roughly the same concentrations. The notion of a "superstructural organization" to the response space, determined by the relative chemical properties of the analytes, has been examined by a number of authors, most prominently Lewis and co-workers in the context of carbon black-polymer composite chemiresistors [11], and Grate and co-workers in the context of elasto- meric thin films on surface acoustic wave sensors [12]. These authors have demonstrated gross spatial separations amongst VOCs in the 2-D PCA subspace with respect to hydrogen bonding characteristic and dipole moment.

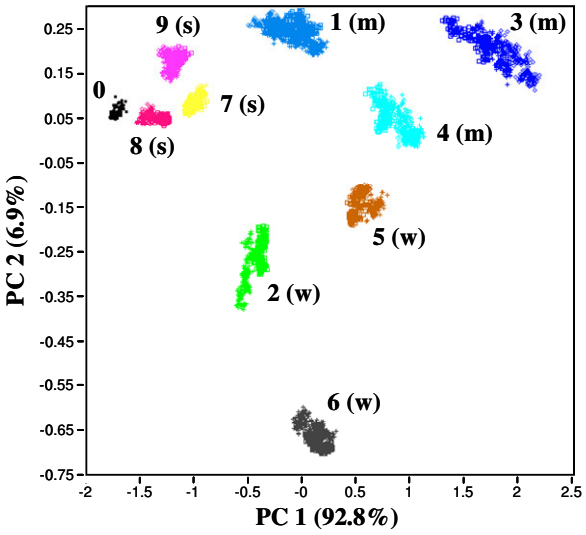

Fig. 2. Two-dimensional, principal components analysis (PCA) plot of cantilever deflection responses to several VOCs.

A similar comparison is shown in Fig. 2, with (w)eakly, (m)oderately, and (s)trongly hydrogen bonded solvents labeled accordingly. While our simplistic analysis reveals some tantalizing relationships in the data – for example, the rough grouping of aromatic, and cyano- and halo-substituted hydrocarbons, all exhibiting poor hydrogen bonding – a more analytical approach is required to select polymers that maximize chemoselectivity in cantilever deflection response. Our initial work toward this goal is briefly discussed in the final section (Section 4).

3.2 Sensor Array Performance

With a chemical signature library created within the 2-D PCA subspace, detection tests were conducted to gauge the performance of the sensor array, particularly with respect to the reproducibility of response. Analytes at concentration values corresponding to the training data were selected at random to be exposed to the device. During these "live" exposure experiments, the collection of six differential deflection voltages was projected into the 2-D PCA subspace as a cursor, updating every three seconds as the composition of the vapor stream changed; this scheme permitted visual tracking of the analyte identification (ID) process in near-real-time. Note that the PCA plot was not recomputed at each time step to include the detection information, but was based solely on the prior training data; this was to prevent modification of the signature library in the event of an exposure to an unknown species.

Upon first exposure to an analyte vapor, the onset of bending is nearly instantaneous. The time to full sorption by the six polymer set, and hence maximum cantilever deflection, varies with analyte. For example, acetonitrile at ~7200 ppm, requires approximately 60 seconds for positive ID – that is, the live cursor arrives at the centroid of the PCA cluster ("5" in Fig. 2). However, identification with high confidence can be made well before equilibrium is achieved; in this case, the live cursor approaches the centroid of the acetonitrile cluster to within about three standard deviations in ~30 seconds or less.

In some cases, particularly at higher concentrations of analyte, the sorbed analyte causes a plasticization of the glassy polymer, evidenced by a cusp in the deflection signal (Fig. 3, dashed circle). The concentration threshold at which this occurs varies with analyte, polymer, and thickness of the polymer film. The plasticization is inferred from the significant alteration of the "zero analyte" baseline voltage immediately after the VOC is removed from the vapor stream, and confirmed as this baseline slowly returns to its pre-exposure levels.

This apparent hysteresis is obviously undesirable from the standpoint of chemical identification. However, for the set of analytes that we have trained against, the apparent transition of the polymeric sensor elements to the rubbery regime and a return to the original glassy condition seems to be fully reversible, provided there is sufficient purging by dry, inert gas following an exposure.

Since the onset and duration of an analyte exposure under actual operating conditions will not be deliberately parsed as in our artificial detection tests, the use of pre-programmed, periodic purge cycles will help eliminate this phenomenon.

4 PREDICTIVE INTERACTION MODELS

The chemoselectivity of "electronic nose" arrays is predicated on the cross-reactivity of each sensor element; that is, each sensor element must react differently and with a broad variation in magnitude to the set of analytes, such that the number of possible, unique response patterns across the array is very large in number. To maximize this diversity (and concomitant discrimination) for sensors based on sorptive polymers, the polymers must be carefully

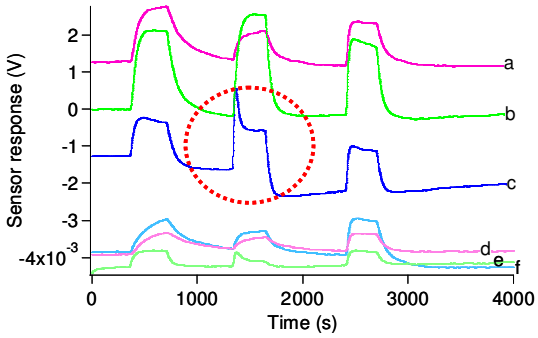

Fig. 3. Plots of cantilever deflection voltage versus time for six polymer-coated cantilevers (a-f) upon exposure to three different analytes. The dashed circle indicates a polymer that has undergone softening upon analyte exposure. Note that the polymer slowly returns to the glassy state, as evidenced by the recovering baseline.

selected based on their chemical and physical interactions with the analytes of interest.

In an effort to go beyond a trial and error approach, various theoretical or semi-empirical models have been used to try and predict the degree of sorption of organic vapors by polymers [13-15]. The partition coefficient K, describing the idealized dissolution of a vapor into a polymer, is a theoretical parameter that is simple to compute and which can be readily compared to our experimental deflection data. We have adopted the usage of K_{rel}, as in Ref. 12, which is a relative partition coefficient assessing the degree of sorption of various analytes with respect to a particular polymer. A plot of K_{rel} versus experimental deflection voltages in shown below for one of our six polymers (a homopolymer: molecular weight = 75 kDa, T_g = 119°C) (Fig. 4).

For this polymer, the overall trends in cantilever deflection generally follow those predicted for equilibrium sorption across our test set of nine analytes. This correspondence is less successful for the other polymers, which includes two terpolymers and possess a range of molecular weights, glass transition temperatures, and side-chain polarities. Although direct proportionality between vapor sorption and sensor response has been shown for polymer-based chemiresistor sensors [11], our investigations reveal no such simplistic relationship for polymer-based cantilever sensors, where a chemical to mechanical transduction occurs. We are currently working on developing a model to bridge the functional gap between VOC sorption and the resultant deflection of the polymer-coated cantilevers; such a model will account for several factors, including: 1) the degree of volumetric strain that results from a given degree of solvent permeation; 2) the transmission of surface stress at the polymer/cantilever interface, in a non-point loading and non-slipping regime; 3) bending of a heterogeneous, laminate cantilever (measured at less than 2.5 µm for the high analyte concentrations examined in this work) in the limit of modest deflections with respect to the nominal radius of curvature.

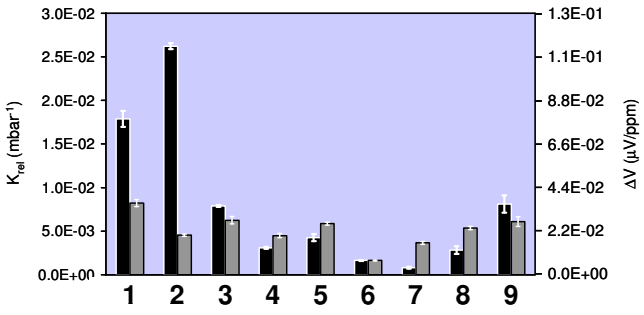

Fig. 4. Column plot of K_{rel} (black; $mbar^{-1}$) and scaled deflection response ΔV (gray; µV/ppm) for representative polymer sorption of nine VOCs (as numbered in Section 3.1)

5 FUTURE WORK

A resistive heater will be incorporated into each cantilever in the next generation sensor to thermally enhance desorption during purge cycles; by periodically driving off residual analytes, the primary source of calibration drift (with respect to the agent signature library) can be wholly eliminated. A transition from thermoplastic to cross-linked polymers is also planned, to provide greater mechanical stability to the sensor films against plasticization. For long-term deployment applications in humid or corrosive environments, covalent linkage of the polymer coatings to the cantilever substrate will help prevent creep and delamination.

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